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Procedure for Dyeing Textile Materials of Polyacrylonitrile

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(3 patent applications submitted in Great Britain in the name of the applicant: the 1st and 3rd on May 7, 1963, and April 6, 1964, under no. 17,987/1963; the 2nd on November 21, 1963, under no. 46,019/1963)

The present invention concerns a process for dyeing textile materials of polyacrylonitrile, that is, textile materials produced substantially starting from polymers of acrylonitrile or from copolymers obtained with at least 85 % acrylonitrile. As examples of textile materials of polyacrylonitrile, we can mention "Acrilan," "Courtelle," "Orlon," "Crylor," "Dyalon," and "Vonel W," all of which are registered trademarks.

It is known that it is possible to dye textile materials based on polyacrylonitrile with dispersed colorants, basic colorants, and acidic colorants for wool or vat colorants; in practice, dispersed colorants and basic colorants are used to a great extent for this purpose. Nevertheless, the known colorants for polyacrylonitrile have certain inconveniences, dispersed colorants generally having mediocre accumulation properties, so that intense shades cannot be obtained in an economical manner, and basic colorants have mediocre properties of equalization.

The applicant has now found that certain colorants based on benzylidene oxindole have excellent dyeing and stability properties on textile materials based on polyacrylonitrile.

According to the invention, a textile material of polyacrylonitrile is dyed with a dye having as its formula:

[diagram]

Formula I

in which A is hydrogen or a lower alkyl radical, B is hydrogen or a simple substituent, R_1 is a lower alkyl radical or substituted lower alkyl radical, R_2 is hydrogen, a lower alkyl radical, or a substitute lower alkyl radical, R_3 is hydrogen or a simple substituent, and the expression "lower" indicates a radical having no more than 5 carbon atoms, whereby the colorant molecule lacks sulfonic-acid and carboxylic-acid groups.

As examples of simple substituents that can be represented by B, we can mention halogen atoms, lower alkyl or alkoxy radicals, and nitro or amine radicals. As simple substituents that can be represented by R_3, we can mention halogen atoms, or lower alkyl or alkoxy radicals.

As examples of substituted lower alkyl radicals that can be represented by R_1 and R_2, we can mention the lower alkyl radicals substituted with halogen groups (for example, chloro or bromo), cyano, hydroxy, acyloxy (for example, acetoxy and ethoxy), carboxy, aminocarbonyl (including alkyl and dialkyl-aminocarbonyl groups, for example, methylaminocarbonyl and diethylamino-dicarbonyl), carbalkoxy (for example, carbethoxy) and methyloxy.

The colorants used in the process of the present invention can be obtained by condensing oxindole or one of its substituted derivatives in an appropriate manner with an aldehyde having as its formula:

[diagram]

Formula II

[illegible]

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in which R_1, R_2, and R_3 have the same meanings as above. Condensations of this type have been described by Wahl and Bagard in *Comptes Rendus*, vol. 149 (1909), pages 132 through 134, and in *Bulletin de la Société Chimique de France*, fourth series, volume 5 (1909), page 1037.

The colorants can be applied to textile materials based on polyacrylonitrile starting from an aqueous dispersion, stabilized, if desired, by the presence of dispersion agents, which can be of the anionic, non-ionic, or cationic type, for example, condensates of formaldehyde, phenol or naphthol and sulfonic acid, polyetheneoxy-derivatives of phenols or amines, or alkyl ammonium salts with long chains. Dyeing can be done by known processes for the application of dispersed colorants to textile materials based on polyacrylonitrile, for example, by progressively increasing the temperature of the bath, for example, to at least 80 °C and preferably to the boiling point, and maintaining this temperature until the dyeing is complete. If desired, the dyeing can be done under a pressure greater than atmospheric pressure at a temperature higher than 100 °C, for example, between 110 and 120 °C. Colorants can be applied in a mixture with other dispersed colorants, if desired.

According to one variant, colorants of formula I can be applied to textile materials of polyacrylonitrile starting from acidic baths under conditions currently used for applying basic colorants to textile materials of polyacrylonitrile. Usually, the colorant of formula I is applied in the form of a paste in a 30% aqueous solution of acetic acid, to obtain a reserve liquor that is added to a desired quantity of water to form a dye bath, starting from which the textile material can be dyed, for example, between 80 and 120 °C, preferably at or near the boiling point, or at higher temperatures under pressure, if desired. Under these conditions, the colorants can be applied in a mixture with known basic colorants. Other acids can be used, for example, hydrochloric acid, formic acid, chloroacetic acid, sulfuric acid, and phosphoric or sulfamic acid, instead of the acetic acid, if desired.

Thick printing pastes containing the colorants and the acid can be applied, if desired, to textile materials of polyacrylonitrile by one or another of the known techniques for printing textiles.

After the dyeing or printing, the textile material can be rinsed in water and treated with a tepid solution of a synthetic detergent, in order to remove any dye that is weakly adhering to the surface.

The dyeings and printings obtained have a shade ranging from yellow to orange, according to the chemical composition. The colorants have a good affinity in regard to textile materials of polyacrylonitrile, accumulating perfectly to give intense, deeper, shades, and they have excellent equalization properties. They likewise have good properties of stability, especially to washing, to light, and to the formation of folds in steam.

In the process of the invention, it is preferable to use colorants of Formula I in which A represents hydrogen or a lower alkyl radical, R_1 represents a beta-cyanoethyl radical, R_2 represents a lower alkyl or beta-cyanoethyl radical, and B and R_3 each represent a hydrogen atom. These colorants, which form new compounds and themselves form an additional peculiarity of the present invention, give brilliant yellow shades that have excellent stability to washing, to light, and to the formation of folds in steam. They can be prepared by condensing oxindole or an N-(lower alkyl)- oxindole with an aldehyde corresponding to Formula II, in which R_1, R_2, and R_3 have the meanings given in this paragraph.

British patent no. 616,385 of September 2, 1946, describes the dyeing of an object including a polymer of acrylonitrile with a colorant of the methine series, which excludes groups of carboxylic acid or sulfonic acid or with the free base corresponding to such a colorant. In comparison with the colorants described in the cited British patent no. 616,385, the colorants of the present invention are superior in regard to their properties of equalization, when they are applied to textile materials of polyacrylonitrile.

The following examples are given as non-limiting illustrations of the invention, and the parts are by weight.

Example 1. — A dye bath is prepared containing 5 parts of 3-(4'-dimethyl-aminobenzylidene)oxindole, 5 parts of sodium cetyl and oleyl sulfate, and 7.5 parts of the condensation product of formaldehyde and naphthalene sulfonic acid (sodium salt) in 10,000 parts of water. The temperature of the dye bath is brought to between 50 and 60 °C, and 500 parts of a textile material based on polyacrylonitrile is introduced. The temperature is increased progressively to 100 °C, and the dyeing is continued at this temperature for 90 minutes. The dye bath is then cooled slowly, and the textile material is removed,

rinsed in water, treated for 15 minutes at 50 °C in a solution of 2 parts of the condensation product of nonyl phenol and ethylene oxide in 1,000 parts of water, rinsed again, and dried.

The dyed textile material has a uniform brilliant yellow shade, and has good stability to washing and to light.

Example 2. – Five parts of 3-(4'-dimethyl-aminobenzylidene)-oxindole in 10 parts of a [illegible]% aqueous solution of acetic acid. The reserve liquor obtained in the way is added to 10,000 parts of tepid water, to form a dye batch, into which 500 parts of a textile material of polyacrylonitrile are introduced. Dyeing is then done at 100 °C for 90 minutes. The bath is cooled slowly, and the textile material is removed, treated for 15 minutes at 50 °C in a solution of 2 parts of a synthetic detergent in 1,000 parts of water, rinsed again, and dried.

The textile material is dyed with a uniform brilliant yellow shade and has good stability to washing and to light.

Example 3. – A printing paste is prepared by dissolving 2 parts of 3-[4'-(N'-beta-cyano-ethyl-N'-methylamino)-benzylidine-]N-ethyloxindole in 28 parts of water, and the solution is agitated in 70 parts of a thickener containing 6 parts of sodium alginate, 2 parts of an aqueous emulsion of sulfonide of spermaceti oil, and pine oil, 2 parts of m-nitrobenzene sodium sulfonate, 10 parts of urea, and 50 parts of water.

The printing paste is applied by means of engraved rollers to a textile material of polyacrylonitrile, and a dry printing is obtained thereby; it is then evaporated between 100 and 105 °C for 30 minutes. The printed material is then rinsed in water, treated for 10 minutes at 50 °C in a solution of 2 parts of a synthetic detergent in 1,000 parts of water, rinsed again, and dried.

A brilliant yellow shade is obtained, which has good stability to washing and to light.

The following table gives other examples of colorants that can be applied to textile materials based on polyacrylonitrile by any of the processes described in examples 1, 2, and 3. The colorants correspond to general Formula I, with the substituents indicated. All have excellent equalization properties.

[table] [see original]
[left column] Example
[right column]

Example	Shade of polyacrylonitrile
4	Yellow
5	Reddish yellow
7	Yellow
14	Reddish yellow
15	Yellow
16	Reddish yellow
17	Yellow
18	Reddish yellow
21	Yellow
22	Reddish yellow
25	Yellow

[left column, heading] Example
[right column]

31	Reddish yellow
32	Orange-yellow
34	Yellow
38	Reddish yellow
39	Yellow
41	Yellow-orange
42	Yellow
43	Yellow-orange
46	Yellow
48	Reddish yellow
50	Yellow
52	Reddish yellow
56	Orange-yellow
57	Yellow
59	Reddish yellow
65	Orange-yellow
68	Reddish yellow
71	Yellow

The following examples illustrate the production of the preferred colorants of the present invention.

Example 74. – 4.2 parts of piperidine are added to a solution of 13.3 parts of oxindole and 18.8 parts of p-N-beta-cyanoethyl N-methyl aminobenzaldehyde in 100 parts of ethanol, and the mixture is heated under reflux for 1 hour. After cooling, the solution deposits 28 parts of 3-[4'-N-beta-cyanoethyl-N-methyl amino)-benzylidene] oxindole in the form of orange prisms having a melting point between 210 and 211 °C.

Example 75. – Using 16.1 parts of N-ethyl oxindole in place of the oxindole of Example 74, 80 parts of 3-[4'-(N-beta-cyanoethyl-N-methylamino)-benzylidene]-N-

ethyl oxindole are obtained, having a melting point between 136 and 137 °C.

Example 76. – Using 14.7 parts of N-methyl oxindole in place of the oxindole of example 73, 29 parts of 3-[4'-(N-beta-cyanoethyl-N-methylamino)-benzylidene]-N-methyl-oxindole are obtained.

Example 77. – Using 20.2 parts of p-N-beta-cyanoethyl N-ethyl aminobenzaldehyde in place of the p-N-beta-cyanoethyl-N-methyl aminobenzaldehyde of Example 74, 25 parts of 3-[4'-(N-beta-cyanoethyl-N-ethylamino) benzylidene]-oxindole are obtained, having a melting point between 159 and 160 °C.

Example 78. – Using 23 parts of p-N-beta-cyanoethyl N-n-butyl aminobenzaldehyde in place of the p-N-beta-cyanoethyl-N-methyl-aminobenzaldehyde of Example 74, 24 parts of 3-[4'-(N-beta-cyanoethyl-N-n-butyl-amino)-benzylidene] oxindole are obtained, having a melting point between 148 and 150 °C.

Example 79. – Using 22.7 parts of p-N,N-bis(beta-cyanoethyl)aminobenzaldehyde in place of the p-N-beta-cyanoethyl-N-methyl-aminobenzaldehyde of Example 74, 31 parts of 3-[4'-N,N-bis(beta-cyanoethyl) aminobenzylidene]-oxindole are obtained, having a melting point between 218 and 220 °C.

Example 80. – Using 16.1 parts of N-ethyl oxindole in place of the oxindole of Example 79, 33 parts of 3-[4'-N,N-bis(beta-cyanoethyl)-aminobenzilydene] N-ethyloxindole are obtained, having a melting point between 154 and 155 °C.

SUMMARY

A. A process for dyeing textile materials based on polyacrylonitrile, characterized by the following points, separately or in combinations:

1. A colorant having as its formula:

[diagram]

is used, in which A is hydrogen or a lower alkyl radical, B is hydrogen or a simple substituent, R_1 is a lower alkyl radical or a substituted lower alkyl radical, R_2 is hydrogen or a lower alkyl radical or substituted lower alkyl radical, R_3 is hydrogen or a simple substituent, and the term "lower" indicates a radical having no more than 5 carbon atoms, whereby the colorant molecule contains no sulfonic-acid or carboxylic-acid groups;

2. B represents a halogen atom, a lower alkyl or alkoxy radical, or a nitro or amino radical;

3. R_3 represents a halogen atom or a lower alkyl or alkoxy radical;

4. R_1 represents a lower alkyl radical substituted with a halogen, cyano, hydroxy, acyloxy, alkoxy, carboxy, amino, carbonyl, carbalkoxy, or mesyloxy group;

5. R_2 represents a lower alkyl radical substituted with a halogen, cyano, hydroxy, acyloxy, alkoxy, carboxy, amino, carbonyl, carbalkoxy, or mesyloxy group;

6. The colorant is applied starting from an aqueous dispersion at a temperature between 80 and 100 °C;

7. The colorant is applied starting from an aqueous dispersion at a temperature between 80 [°C] and the boiling point;

8. The colorant is applied starting from an acid dye bath at a temperature between 80 and 120 °C.

B. As a new industrial product, colorants corresponding to the formula:

[diagram]

in which A represents hydrogen or a lower alkyl radical, R_1 represents a beta-cyanoethyl radical, R_2 represents a lower alkyl or beta-cyanoethyl radical, and R_3 and B represent hydrogen atoms.

C. A production process for colorants according to paragraph B, characterized by the fact that it consists of condensing oxindole or an N-(lower alkyl) oxindole with an aldehyde having as its formula:

[diagram]

in which R_1 represents a beta-cyanoethyl radical, R_2 represents a lower alkyl or beta-cyanoethyl radical, and R_3 represents hydrogen.

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